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# Use of Ultrasonics in the Rapid Extraction of Hi-vol Filters for Benz-a-pyrene (B&P) Analysis

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16. ABSTRACT

A rapid simple procedure was developed to extract residual Benzo-a-Pyrene from a single hi-vol filter strip. It involves quantitative dispensing of cyclohexane, 10 minutes of ultrasonication at 78C and a quiescent period of 1 hour. At that time the solvent is ready for chromatography.

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# USE OF ULTRASONICS IN THE RAPID EXTRACTION OF HI-VOL FILTERS FOR BENZ-a-PYRENE (BaP) ANALYSIS

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## INTRODUCTION

For many years the particulate material collected on glass-fiber filters from high-volume (hi-vol) air samplers has been analyzed for benz-a-pyrene (BaP). The procedure (1), which includes a 6-hour Soxhlet extraction, concentration of the extract, separation by thin layer chromatography (TLC), and detection by fluorescence, is quite lengthy. This paper presents a modification which employs ultrasonics in the extraction, significantly shortening this step. In addition, the concentration step is eliminated and the procedure can be used on a single filter strip with good results.

## EXPERIMENTAL

Approach. Simplex Optimization (2) was applied to the ultrasonic extraction procedure. However, there was no way to formally accommodate an important variable: filter-to-filter variability. An attempt was made to minimize its influence by normalizing the results from several 1-in. strips from each filter to the results obtained in a 6-hour Soxhlet extraction of a single strip. Temperature and duration of sonication were chosen as Simplex Optimization variables. Another variable - the length of time between sonication and spotting on the TLC plate - was also found to influence the results and was evaluated independently of Simplex.

Equipment.* A Perkin-Elmer Model MPF-44-B Fluorescence Spectrophotometer with a Thin Layer Plate Scanning Attachment, a Perkin-Elmer Model 048 Digital Integrator, and a Perkin-Elmer Model 56 Recorder were used for all measurements from the TLC plates. The slit opening on the scanning attachment was modified to cover the full width of the 1 cm channel on the TLC plate. The sonicator was a 980-watt unit obtained from Heat Systems Ultrasonics. The 20-cm x 20-cm plates were coated with a 250-μm layer of 20% acetylated cellulose (Analtech, Inc.) and scored into 18 channels, each 1 cm wide, with a Schoeffel plate-scoring apparatus. Samples and standards were simultaneously applied to the plate from 100-μL Teflon$^R$-coated blunt-tip syringes with an 18-position Analytical Instrument Specialities TLC plate multispotter. Filter strips were extracted in 24-mL glass vials with Teflon$^R$-lined screw caps. All work was done under Kodak Yellow Chrom II$^R$ filters to protect the samples from light.

Chemicals.* Spectroquality cyclohexane, ethanol, and methylene chloride were obtained from Burdick and Jackson Company or Fisher Scientific Company. The BaP (Aldrich Chemical Company) had been recrystallized in the EPA laboratory by Dr. Eugene Sawicki. BaP calibration standards were prepared in cyclohexane in the following concentrations:

100 ng BaP/mL
70 ng BaP/mL
40 ng BaP/mL
20 ng BaP/mL
10 ng BaP/mL

Small quantities of each standard were transferred to Teflon$^R$-capped vials, frozen, and stored in the dark until used.

## ANALYTICAL PROCEDURE

Sample Preparation. A 1-in. x 8-in glass-fiber strip was folded and placed in the bottom of the 24-mL vial. An 8-mL volume of cyclohexane was dispensed into the vial and the cap was screwed on "finger tight." The vial was placed in a rack in the sonicator with the water level of the bath about 0.5 in. above the cyclohexane level in the vial. The sonicator was operated for 10 min. with the bath temperature at 78-79 °C. To facilitate interphase mass transport, samples were allowed to sit undisturbed at room temperature for 1-hour before spotting on a plate.

Plate Spotting, Development, and Reading. A set of calibration standards was removed from the refrigerator and allowed to warm to room temperature. A scored plate was placed in an oven at about 50 °C for at least 10 minutes immediately prior to spotting. The syringes were loaded above the 100-μL mark with the samples and standards, placed in the appropriate order on the multispotter, and the plungers driven to the 100-μL mark. The syringe tips were blotted off with filter paper. The plate was placed in position and the syringe plungers driven to the 20-μL mark. The spot size was minimized by driving the plungers in short, quick bursts and allowing the solvent to evaporate between bursts.

No more plates were prepared than could be quantitated in one day. The order of quantitation was the order of preparation. The series of channels was spotted so that the following sequence of data was obtained: Two spottings of each standard were applied to the plate in random order in the first 10 channels; the quality control (the 40 ng/mL standard) was applied in the 11, 17, 23,... channels. The remaining groups of 5 channels were used for sample extracts. When the spots were dry, the plates were developed in TLC tanks in a hood to the 19-cm line using a solvent mixture of 100 mL ethanol and 50 mL methylene chloride. The plates were air dried and placed in the fluorescence spectrophotometer plate scanner. Each channel was scanned for BaP using an excitation wavelength of 386 nm and observing the emission at 429 nm. Excitation and emission slits were set so that the 100-ng/mL standard produced a peak area of about 10,000 counts without any electronic multiplication. (On the MPF-44-B spectrophotometer, the appropriate settings were approximately "3" and "8" for excitation slit and emission slit, respectively.)

*Mention of trade names or commercial products does not constitute endorsement or recommendations for use by the U.S. Environmental Protection Agency.

Computations

$$\frac{\text{ng BaP}}{\text{M}^3\text{ of air sampled}} = \frac{(S)\ (C)\ (R_s)\ (R_f)}{(C_s) \times \text{M}^3\text{ air sampled}}$$

$$= \frac{900\ (S)\ (C)}{(C_s) \times \text{M}^3\text{ air sampled}}$$

Where S = Conc. of BaP standard in nanograms/80 µL
C = Sample integrator counts
$C_s$ = Standard integrator counts
$R_s$ = 100, spotting ratio 80 µL from 8 mL
$R_f$ = 9, filter-to-filter strip exposure ratio 63 sq in. is area of exposed filter and 9 sq. in. is area of exposed filter strip.
$M^3$ = cubic meters

## RESULTS AND DISCUSSION

The results of Simplex optimization were inconclusive except for the clear indication that higher temperatures gave more accurate results. One possible cause of such behavior could have been variable loss of solvent from the vials. Therefore, the loss of mass was measured (Table I) and was found to be unimportant though finite.

The uncertainty in the results obtained from the Simplex procedure was probably due to the failure to control the length of time allowed for the interphase mass transport step. The importance of this step was evident in results from experiments in which the time was controlled (Table II).

Extractions of trace elements from hi-vol filters require on the order of 1-hour of contact time to effect solubilization and interphase mass transport. It is known that glass-fiber filters imbibe large quantities of hot acids. We had assumed that such a process would not occur with cyclohexane. However, these experiments showed that assumption to be incorrect. Since the experimental times and conditions were reasonable and resulted in a great improvement in efficiency, further work was judged to be unnecessary.

Results obtained using the new procedure were compared with results previously obtained using the old one. Portions of each filter in composites from 21 sites were analyzed by the new procedure. The values obtained were averaged for each composite taking any "less than detectable" value as 0. Table III lists the results together with corresponding composite results obtained using the old procedure. Comparison of the two methods by a linear regression in which the variance of the new result is assumed to be 75% of the old yields a relation of: new = 0.205 + 0.897 old. The intercept and slope are not significantly different from 0 and 1, respectively. In addition to demonstrating the comparability of procedures, this satisfactory agreement documents that residual BaP on hi-vol filters stored in file cabinets without special precautions is stable for at least 1 year since that time on the average elapsed between the original and the new determinations.

TABLE I

| Ultrasonication Temp. (°C) | Ultrasonication Time (°C) | Weight of Capped Vial + Filter + Cyclohexane (g) Before Sonication | Before Sonication | Mass Load (g) | Load Cyclohexane(%) |
|---|---|---|---|---|---|
| 77 | 30 | 28.0678 | 27.6784 | 0.39 | 6.3 |
| 78 | 10 | 28.1553 | 27.9927 | 0.16 | 2.6 |
| 78 | 20 | 29.4886 | 29.0631 | 0.43 | 6.8 |
| 78 | 40 | 28.7448 | 27.8849 | 0.86 | 13.8 |
| 79 | 10 | 29.9181 | 29.6564 | 0.26 | 4.2 |
| 79 | 20 | 29.3839 | 29.2953 | 0.09 | 1.4 |
| 80 | 10 | 29.1669 | 28.8889 | 0.28 | 4.5 |
| 80 | 20 | 29.0690 | 29.0496 | 0.02 | 0.3 |

TABLE II

| Time Interval Between Sonication and Plate Spotting (min) | Integrated Counts by Fluorescence Scanning of Developed Spot |
|---|---|
| 10 | 3440 |
| 25 | 3509 |
| 40 | 3538 |
| 55 | 3748 |
| 70 | 3781 |
| 85 | 3779 |
| 100 | 3485 |

TABLE III

| BaP Detected (ng/$M^3$ air sampled) Ultrasonic Method | Soxhlet Method |
|---|---|
| 1.24 | 1.54 |
| 1.70 | 0.92 |
| 4.92 | 4.26 |
| 6.75 | 8.27 |
| 10.40 | 10.79 |
| 2.42 | 2.58 |
| 0.17 | 0.31 |
| 0.14 | 0.09 |
| 1.43 | 0.63 |
| 0.69 | 0.27 |
| 1.02 | 1.07 |
| 0.30 | 0.49 |
| 0.48 | 0.39 |
| 0.65 | 0.66 |
| 0.94 | 1.51 |
| 0.27 | 0.35 |
| 1.64 | 1.02 |
| 1.08 | 0.45 |
| 0.19 | 0.23 |
| 0.92 | 0.57 |
| 2.49 | 2.77 |

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